（第3号様式）(Form No. 3)

学 位 論 文 要 旨
Dissertation Summary

氏　　名 (Name)　: **Novriany Amaliyah**

論 文 名:　: **Reduction of Zinc Oxide Nanoparticles using Microwave In-Liquid Plasma Method**
(Dissertation Title)　マイクロ波液中プラズマ法による酸化亜鉛ナノ粒子の還元

The rise in the demand for oil, its limitations as a non-renewable energy resource as well its effect on global warming has forced the consideration of alternative energy storage and conversion systems. The development of next-generation energy storage devices with high power and high-energy density is a key to the prosperity of electric and hybrid-electric vehicles (EVs and HEVs, respectively), which are expected to replace conventional vehicles if only gradually, and help solve the problems of air pollution and climate change.

In the field of energy storage, the nanotechnological market potential concerns first and foremost, enhanced batteries for portable electronics or hybrid and electric vehicles, nano-optimized supercapacitors and nonporous hydrogen storage materials. The world market for battery materials showed double-digit growth amounting to more than 1.2 billion dollars. Lithium, aluminum, iron, and zinc show great promise for use in air batteries. Among these metals, zinc, particularly as a nanoparticle, has attracted great interest due to its low equivalent weight, abundance, and high energy density. Zinc has received the most consideration as a potential metal-air battery candidate, because it is an electropositive metal that is relatively stable in aqueous and alkaline electrolytes without significant corrosion. It has been used over

many years in commercial primary zinc-air batteries. A promising high-capacity power source for portable applications as well as in larger sizes, such as for electric vehicles, can be achieved through the development of a practical rechargeable zinc-air battery that has an extended life cycle. Moreover, it would also be safe and environmentally friendly.

Zinc-air batteries generate electricity by combining atmospheric air with zinc metal in a liquid alkaline electrolyte with zinc oxide as the resulting byproduct. When the battery is recharged, the zinc oxide turns back into its constituent parts: oxygen and zinc metal. The formation of large quantities of zinc oxide requires a method for recycling the air batteries because it is necessary to balance zinc production with its recycling. The recycling of zinc is a critical and beneficial supplement to its primary metal production in order to decrease energy use and to minimize emission as well as reducing waste materials.

Several morphologies of zinc, such as zinc nanoparticles, zinc nanowires, zinc nanofibers, zinc nanotubes, and zinc nanosheets have been synthesized by various methods, including in-liquid plasma, laser ablation, electromagnetic levitation gas condensation, shortcut hydrothermal strategy, electron cyclotron Resonance (ECR) plasma, ball-milling process, mechanical deformation process using hexagonal Zn oxide powder, simple thermal vapor phase deposition, metalorganic chemical vapor deposition and thermochemical reduction.

Zinc oxide nanomaterial synthesis by zinc oxidation has been reported in numerous studies, but little research has been conducted into its reduction.

Alcohol has been used as reductant in many kinds of metal nanoparticles syntheses such as for platinum, silver, graphene, zinc oxide, titanium, iron oxide, and copper due to the its non-toxic properties and environmental friendly characteristics. Therefore, a combination of alcohol with efficient heating would necessary increase the reduction reaction processes.

When microwave or radio-frequency-induced plasma is generated at the surface of a metallic electrode submerged into a liquid, nanoparticles are synthesized by erosion of the electrode. In-liquid plasma has been successful in the synthesis of many kinds of nanoparticles such as zinc, zinc oxide, tungsten oxide, silver, gold, and magnesium hydroxide just to name a few. By applying plasma to a zinc electrode in an alcoholic solvent, metallic zinc nanoparticles are produced, while, in water, a mixture of zinc and zinc oxide nanoparticles is formed. This suggests that the oxidative or reductive atmosphere of the vapor of the liquid determines the physical properties of the synthesized nanoparticles. Plasma can be observed easily in the vapor, which is generated by the evaporation of the surrounding liquid.

During plasma generation, characteristic Zn lines were detected at 468.0, 472.2, 481.1 and 636.2 nm, and the excitation temperature was approximately 3400 K as estimated from emission intensity of these lines by the Boltzmann plot method.

After plasma irradiation, there is a great reduction as the absorbance decreases. On the short-wavelength side where a Zn peak is assumed to have been observed, the peak height increased during the elapsed time of plasma generation. While on the long-wavelength side where a ZnO peak was observed, the peak height decreased. The Beer-Lambert law predicts that the intensity of an absorption peak is directly proportional to the concentration of the compound.

The TEM images of ZnO nanoparticles before plasma generation were a mixture of rectangular and hexagonal crystals of 50 to 200 nm in length and rods approximately 200 nm in length. After plasma irradiation, a good crystallinity of cubic particle about 30 to 200 nm in diameter is found on the tip of the electrode and other rectangular particles are observed in the residue of ethanol after evaporation. While in methanol, 100 nm of rectangular particles are observed and the amount of particle aggregation is remarkable in the remaining liquid of methanol. Despite the lack of significant difference of particle synthesized after plasma irradiation by the TEM image, hardly any oxygen is detected in comparison to the amount before plasma irradiation. From energy dispersive x-ray spectrometry (EDS) results the mass ratio of oxygen to zinc is reduced from 24% before plasma irradiation to 6% after plasma irradiation in ethanol and 0.46% in methanol.

From the calculation of the chemical potential of ethanol and methanol, reduction of ZnO is predicted by consideration of chemical equilibrium. Thermal equilibrium composition of dominant products when zinc oxide reacts with ethanol and methanol is calculated from JANAF Thermodynamical Tables. The Gibbs energy change of zinc oxidation indicates that a reducing environment occurs if the temperature is higher than 1140 K. At this temperature, oxygen from zinc oxide start to release and bind with CO and H_2, so the production of H_2O and CO_2 increases. At around 1900 K, the mole fraction of CO_2 and H_2O is reduced. Oxide reduction is considered to continue within this temperature range because the mole fraction of O_2 increases at the same time mole fractions of H_2O and CO_2 decrease.

Other methods for zinc recovery have been proposed in many studies. However, these methods have no information regarding the zinc nanoparticle production required for zinc air batteries. This present method provides recycling of zinc nanoparticles with prevention of re-oxidation, because the reaction area is separated from the air by liquid. An additional advantage to this method is the easy collection of the product since the reduced metal remains in the liquid as dispersed particles.

Zinc nanoparticles were synthesized from reduction of ZnO powder by 2.45 GHz microwave using ethanol and methanol as reducing agents. In this method, reduction takes place in the temperature range of 1500 to 2000 K. The mass ratio of oxygen to zinc decreased both in ethanol and methanol from 24% to 6% and 0.46% respectively. Agglomerated particles were observed when using methanol, though the enthalpy required for reduction is lower than that of ethanol. Moreover, the distinctive nanoparticles synthesized by this experiment and the mechanism of synthesis should be clarified in the future to obtain perfect reduction of oxide and synthesize pure metallic zinc nanoparticles. These results therefore open up promising avenues for reduction in nanoparticle size.